Reactions of Nonequilibrium Oxygen Plasmas with Liquid Olefins

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The oxidation of 13 liquid olefins with either high-voltage or radio frequency (RF) glow discharges has been studied. The reactions were carried out by making the oxygen plasma reach the low vapor pressure substrate. Product formation has proved to be selective—epoxides, aldehydes, ketones, and low quantities of carboxylic acids being the most important species. Fragmentation products were only observed in the traps of the RF system for the most volatile olefin of this study. This indicates that, except for this case, the most relevant interaction of this study has been the heterogeneous reaction of the plasma with the liquid. Total conversion, i.e., mass transformed against initial mass of substrate, has been studied as a function of temperature of the liquid and oxygen flow rate in the reactor, this ranging from 15 to 53.6 mmol/hr in the high-voltage system and 13 to 270 mmol/hr in the RF device. The optimum conversions were 27 to 99%. A correlation between these results and the behavior of the $O(^3P)$ population in the discharge allows us to conclude that this is the most relevant species to the oxidation process. A discussion relating the structures of the olefins with the composition of the mixtures produced by the oxidation is also presented.

KEY WORDS: Oxidation of liquid olefins; oxygen cold plasmas; $O(^3P)$.

1. INTRODUCTION

Selective oxidation of hydrocarbons is an important feature in modern industry for it contributes to the manufacture of a great variety of chemical products. Ethylene, propylene, 1,4-butadiene, and other olefins are common starting materials for producing plastics, lacquers, polyesters, glycols, etc. Nevertheless, considerable research is still being devoted to the oxidation of olefins via catalysis,[1-6] selectivity and, sometimes, yields are far from being

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excellent. As an alternative, plasma technology has been applied to the production of both known and new materials in the last two decades. The interaction of plasmas with gases and solids has been studied extensively, leading to numerous syntheses[7] and methods for surface modifications.[8] In the gas-phase systems, the hot primary products normally may undergo consecutive reactions before they are thermalized. For this reason, the selectivity is often limited. On the other hand, in plasma–solid interactions the products remain on the surface of the solid and are exposed to the plasma for a considerable time. Apart from etching, this again might produce various consecutive reactions. On the contrary, far greater selectivities are achieved in heterogeneous reactions of plasmas with liquid surfaces. This is due to the fact that such systems provide rapid quenching of the hot primary products. The consecutive reactions of the plasma–solid interactions are avoided by stirring the liquid; in this way, products are continuously eliminated from the surface layer.

Reactions of oxygen atoms with organic molecules have been reported by a number of investigators. Most published works have been devoted to olefins and aromatic hydrocarbons in the gas phase,[9–20,26,27,30–32] but only a limited number to reactions in the condensed phases,[21–25,28,29,33] including some alkanes. The first studies of oxygen atom addition to hydrocarbons in condensed phases were performed with low-molecular-weight olefins.[21–23] In either case, they have concentrated on the discussions about the pathways for the reactions. Based on product distribution for diverse starting compounds, the intermediacy of triplet diradicals has been proposed by some authors[21,22] while others have formulated an "epoxide-like" transition complex.[23] To our knowledge, there is only a report on the oxidation of one long straight-chain condensed olefin, namely 1-octene, with nonequilibrium plasmas.[24] With the aim of giving a more complete description of these reactions, more species have been selected for studying the addition of $O(^3P)$ atom to them. Total reactivity has been measured as a function of the oxygen flow rate in the reactor and the temperature of the liquid compounds. Several of them have been studied under the same conditions, in order to determine the dependence of their reactivities on their structures.

2. EXPERIMENTAL

The reactions were carried out by making an oxygen cold plasma reach the low-vapor pressure liquid substrate. Two experimental setups were employed, namely, a high-voltage discharge and a radio frequency device.[25,28,33] Figure 1 is a representation of the former. In both cases the reactor is a double-walled glass vessel of ca. 300 ml. In the high-voltage system, it is supplied with two electrodes composed of aluminum and Teflon.
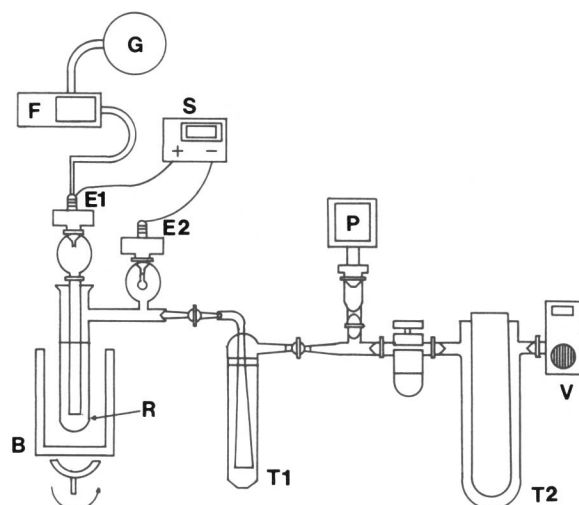
Fig. 1. Schematic of the experimental apparatus. G, gas reservoir; F, flow meter; E1 and E2, electrodes; S, power source; R, reactor; B, cooling bath; P, pressure meter; T1 and T2, traps; V, vacuum pump.

Oxygen is introduced into the reactor through the electrode E1, which is hollow. The plasma is produced by means of a home-made low-frequency high-voltage ac power source that supplied up to 7 kV and 200 mA. The optimum distance between the electrode E1 and the liquid surface for maximum conversion has been found to be 33 cm. In doing this, the oxidation of several hydrocarbons has been carried out by keeping all parameters fixed, except for the length of the reactor R.

In the RF system, the plasma is produced by means of a Branson IPC 100 generator with a fixed frequency of 13.4 MHz and variable power up to 500 W. In order to obtain an efficient coupling of the source to the discharge, a matching box is utilized to connect the generator to the RF coil. This is placed around the reactor approximately 16 cm away from the bottom.

The substrate (2 ml) is placed at the bottom of the reactor and this is cooled down by means of a methanol–liquid nitrogen bath (B in Fig. 1), the temperature being controlled within ± 1°. The liquid is magnetically stirred and the system is connected to a vacuum line equipped with two traps, T1 and T2. These are cooled down with liquid nitrogen and are used to collect any possible volatile product and, hence, to protect the mechanical vacuum pump. The oxygen flow is measured with a 247 B-MKS flow meter and the pressure is monitored with a Leybold-Heraeus TM111 thermotron.

In order to study the $O(^3P)$ population, the light from the discharge was focused onto the entrance slit of a 2.0-m Jarrell–Ash Czerny–Turner scanning spectrometer equipped with a 1808 lines/mm grating. The emission signal was detected by an RCA 4832 photomultiplier that fed a lock-in amplifier, and was finally recorded on a Cole–Parmer pen recorder.

The products of the reactions were identified by means of gas chromatography–mass spectrometry (GC–MS), infrared (IR), and nuclear magnetic resonance (NMR) spectroscopies. A HP 5995 mass spectrometer that utilizes a HP 2671G processor was used. The gas chromatograph was equipped with a 25-m fused silica capillary column. The mid-IR spectra were taken on a Perkin Elmer FTIR model 1700X spectrometer fitted with a Spectra-Tech "Collector" diffuse reflectance accessory, with an accumulation of 10 scans at $4\,cm^{-1}$ resolution. The NMR spectra were taken on a JEOL ECLIPSE 270 MHz spectrometer. Aldrich p.a. products were used as standards.

3. RESULTS AND DISCUSSION

Thirteen olefins have been oxidized using reaction systems activated with either high-voltage or RF discharges. For each substrate, volume and applied power have been maintained constant. As expected, the olefins have shown to be more reactive than the alkanes and the aromatic compounds previously studied.[25,33]

3.1. 1-Decene

A RF plasma was used to oxidize 1-decene. The applied power was 100 W and the time of reaction was 30 min for 2 ml of liquid. The total percentage of conversion, i.e., mass transformed against initial mass of 1-decene, is plotted in Fig. 2 as a function of oxygen flow rate. The temperature of the liquid was fixed at $-65°C$, i.e., 1.3° above its freezing point. The oxygen flow rate at maximum 1-decene conversion was ca. 53.6 mmol/hr (20 sccm). The situation is very similar to those reported for toluene,[28] n-hexane, and n-heptane,[25] and several other aromatic compounds,[33] the reactivity decreasing when the pressure is either lower or higher than the optimum range. The main products have been identified as 1,2-epoxidecane and decanal, which amount to 85% of the total yield. The total by-products are a mixture of 2-decanone and decanoic acid. As for the rest of the olefins, the IR spectrum of the products revealed the following prominent stretching signals (cm^{-1}): epoxidic C–O at 1265; C=O at 1730; O–H at 3500. This was rather weak because of the low amount of carboxylic acid. The most important $[^{13}C]NMR$ chemical shifts (ppm) were: 47 and 52, corresponding to the
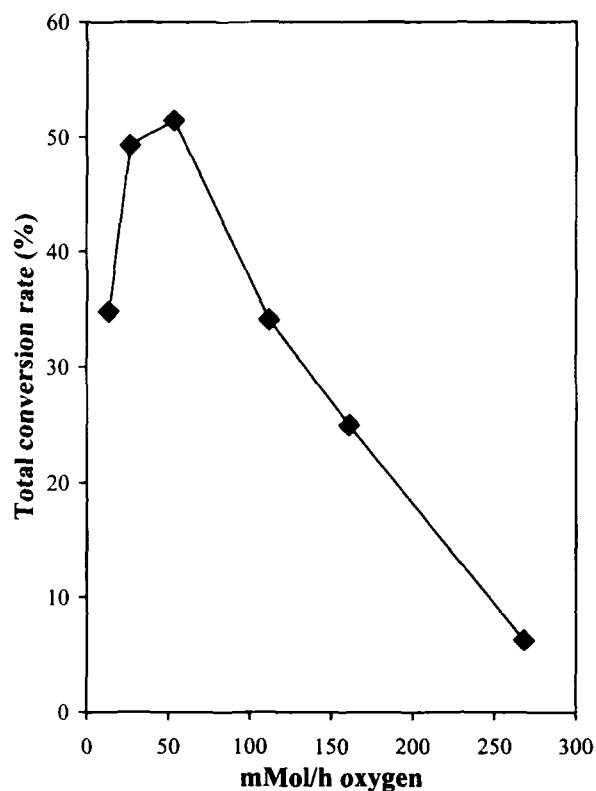
Fig. 2. Conversion rate of 1-decene as a function of the O_2 flow. The temperature of the liquid was −65°C and the power was 100 W. Time of reaction was 30 min. Each point is an average of three individual runs.

CH_2 and CH bonded to the epoxidic oxygen, and 2O2, corresponding to the aldehydic carbon.

3.2. 2-Methyl-1-nonene

2-Methyl-1-nonene was also oxidized by means of a RF oxygen plasma. The applied power was 100 W and the time of reaction was 30 min for 2 ml of liquid. The behavior of 2-methyl-1-nonene conversion rate against oxygen flow rate is presented in Fig. 3. The temperature of the liquid was fixed at −64°C, that is 0.8° above its freezing point. The oxygen flow rate at maximum conversion was ca. 53.6 mmol/hr (20 sccm). The main products have been identified as 2-methyl-1,2-epoxinonane and 2-methyl-nonanal, which amount to 82% of the total yield. The total by-products are a mixture
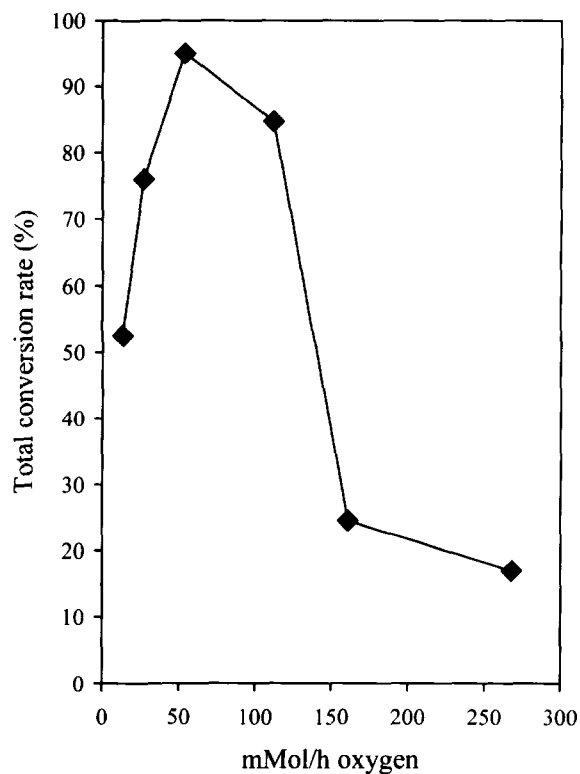
Fig. 3. Conversion rate of 2-methyl-1-nonene as a function of the O_2 flow. The temperature of the liquid was $-64°C$ and the power was 100 W. Time of reaction was 30 min. Each point is an average of three individual runs.

of 2-methyl-nonanone, 2-methyl-nonanoic acid, 2-methyl-nonanol, and 2-methyl-nonane.

3.3. 1-Dodecene

The oxidation of 1-dodecene was carried out using a high-voltage oxygen plasma. The applied power was 35 W and the time of reaction was 30 min for 2 ml of substrate. The total percentage of conversion of 1-dodecene is plotted in Fig. 4 as a function of the oxygen flow rate and the temperature of the liquid. This is the first time we have simultaneously changed these two parameters instead of fixing one of them. This has produced a response surface that shows, in a better manner, the dependence of
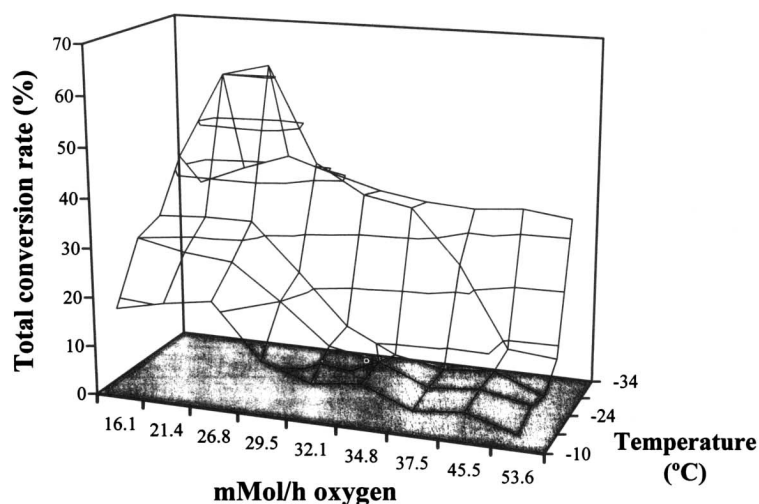
Fig. 4. Conversion rate of 1-dodecene as a function of its temperature and O_2 flow. The applied power was 35 W. Time of reaction was 30 min. Each point is an average of three individual runs.

the conversion with the two variables. The shape of the surface is very similar to those of the plots reported for n-hexane and n-heptane,[25] and 12 aromatic compounds.[33] The maximum conversion was obtained at an oxygen flow rate of 27 mmol/hr (10 sccm), giving a pressure of 0.29 Torr, and −32°C. This temperature is close to the freezing point of 1-dodecene, which is −34°C. The main products have been identified as 1,2-epoxidodecane, and dodecyl aldehyde, which amount to 92% of the total yield. The by-products are a mixture of 2-dodecanone and dodecanoic acid.

3.4. 1-Tetradecene

The oxidation of 1-tetradecene was carried out under similar conditions as those for 1-dodecene. Its total percentage of conversion is plotted in Fig. 5 as a function of the oxygen flow rate and the temperature of the liquid. The response surface shows that maximum reactivity was obtained at an oxygen flow rate of 27 mmol/hr (10 sccm), giving a pressure of 0.29 Torr, and −11°C, just 1° above the freezing point. This is the first time that such a result is observed at nearly room temperature. The main products have been identified as 1,2-epoxitetradecane and tetradecyl aldehyde, which amount to 88% of the total yield. The total by-products are a mixture of 2-tetradecanone and tetradecanoic acid.
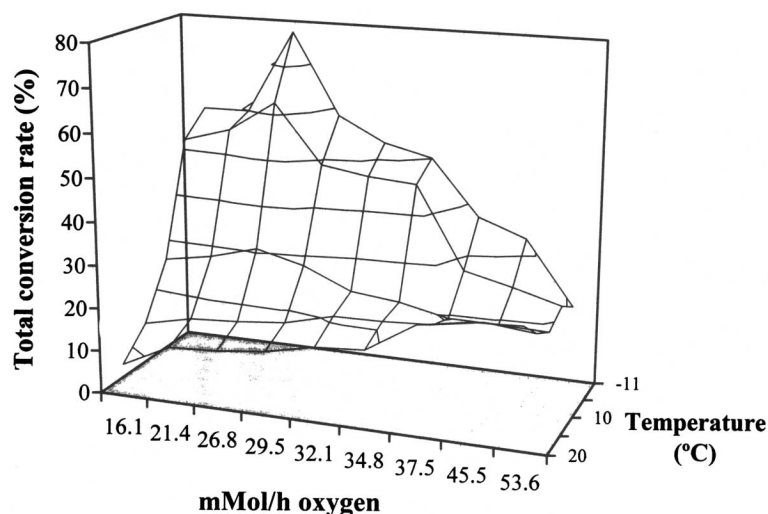
Fig. 5. Conversion rate of 1-tetradecene as a function of its temperature and the O_2 flow. The applied power was 35 W. Time of reaction was 30 min. Each point is an average of three individual runs.

The explanation for the variation of the reactivity of oxygen plasmas with liquid olefins versus oxygen flow rate is the same as that given earlier for liquid n-alkanes.[25] For the sake of completeness, we reproduce it here. At low oxygen pressures the production of $O(^3P)$ in the plasma through the process

$$O_2 + e^- \rightarrow O + O + e^- \tag{1}$$

decreases, since there are less oxygen molecules that can suffer electronic impact (O may be ^3P, ^1D, ^1S, etc.). At the side of higher pressures, because of the higher concentration of O_2 in the plasma, the frequency of collisions between these species and the electrons increases. This implies that the electrons do not have time to be sufficiently accelerated by the electric field and, hence, most of them do not acquire high enough energy to produce the dissociation of O_2, thus generating less $O(^3P)$ atoms. The region of optimum oxygen pressure is obviously a compromise between the two tendencies. This behavior was demonstrated by following the relative population of O I ($2p$ ^3P). This can be correlated to the $3p$ $^3P \rightarrow 3s$ ^3S ($\lambda = 844.6$ and 844.7 nm) transition. The glass reactor was modified by fitting a window to it in order to focus the light from the discharge into the entrance slit of the Jarrell–Ash spectrometer. The signal of O I was recorded and plotted versus the

oxygen pressure in the reactor.[25] The whole vacuum system had to be simplified in order to place the reactor in front of the spectrometer. This is perhaps the reason why the region of optimum oxygen pressure for maximum signal (~0.06 Torr) does not exactly match the one for the maximum conversion of the compounds, but the behaviors presented in Figs. 2–4 are very similar to that of the oxygen signal shown in Ref. (25).

It is important to note that peroxides were not observed among the oxidation products, thus indicating that, under the oxygen pressures of our experiments, the population of $O_2(^1\Delta_g)$ is negligible.[34] In fact, under the same conditions used for $O(^3P)$, an attempt to monitor the population of $O_2(^1\Delta_g)$ was made. This can be correlated to the intensity of the 0, 0 band of the O_2 atmospheric system $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ at 759.4 nm. Nevertheless, although we have recorded the resolved structure of this band at oxygen pressures higher than 2 Torr, it has not been observed at the range of pressures of this study. In addition, singlet oxygen may be deactivated at the liquid surface through the process

$$O_2(a^1\Delta_g) + M \rightarrow O_2(X^3\Sigma_g) + M \qquad (2)$$
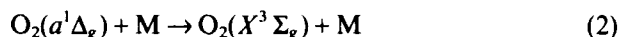
For the sake of completeness, the role of ozone in the oxidation system has been investigated. The ozone generation was negligible at the oxygen flow rates shown in Table I. Its maximum production has been measured at an oxygen flow rate of ca. 82 mmol/min for the high-voltage system and 340 mmol/min for the RF device. Under these conditions, we have passed the O_3 into a solution of the olefins in carbon tetrachloride. The evaporation of CCl_4 left ozonide, a viscous unstable oil, which, in turn, treated with water produced the cleavage into formaldehyde and another carbonylic compound, an aldehyde or a ketone, depending upon the structure of the starting alkene. Part of the formaldehyde produced formic acid, as clearly indicated by a strong signal in the [13C]NMR spectra at 165 ppm. In these spectra, we did not observe the [13C]NMR signals at 47 and 52 ppm, corresponding to the CH_2 and CH bonded to the epoxidic oxygen, as observed for the oxidation with $O(^3P)$. We have not observed the C–O stretching at 1265 cm^{-1} in the IR spectra.

The explanation for the behavior of the reactivity versus temperature, as shown in Figs. 3 and 4, has been given elsewhere.[25] From the point of maximum conversion to higher temperatures, the vapor pressure of the substrate increases. Therefore, these molecules, much bigger than O_2, compete advantageously with it for the electrons and the amount of $O(^3P)$ in the plasma decreases. This explains why the conversion of the hydrocarbon decreases. If the temperature of the hydrocarbon is set much higher, then collisions between electrons and these molecules dominate the plasma and fragmentation plus condensation products, arising from oxygen-free organic

Table I. Reactions of Several Olefins with Oxygen Plasmas

Substrate T(°C)	Source, power (W)	Oxygen flow rate (mMol/h)	Total conversion[a] (%)	Products (%)
1-Tetradecene −11	hv, 35	27.0	77.4	1,2-Epoxitetradecane (51.8); tetradecanal (36.3); by-products[b] (11.9)
1-Dodecene −32	hv, 35	27.0	62.5	1,2-Epoxidodecane (46.2); dodecanal (45.7); by-products[b] (8.1)
2-Methyl-1-nonene −64	RF, 100	111.7	99.3	2-Methyl-1,2-epoxinonane (48.9); 2-methyl-nonanal (33.0); 2-nonanone (9.1); by-products[b] (9.0)
2-Methyl-1-octene −78	RF, 100	111.7	98.1	2-Methyl-1,2-epoxioctane (48.8); 2-methyl-octanal (27.9); 2-octane (9.5); by-products[b] (13.8)
2-Butyl-1-hexene −85	RF, 100	111.7	86.3	2-Butyl-1,2-epoxiohexane (48.8); 2-butyl-hexanal (27.9); 5-nonanone (9.5); by-products[b] (13.8)
2-Ethyl-1-octene −90	RF, 100	111.7	84.3	2-Ethyl-1,2-epoxioctane (50.0); 2-ethyl-octanal (22.5); 2-nonanone (5); by-products[b] (22.5)
3-Ethyl-1-heptene −90	RF, 100	111.7	83.5	3-Ethyl-1,2-epoxiheptane (61.5); 3-ethyl-heptanal (32.6); 3-ethylhexanal (2.5); by-products[b] (3.4)
4-Nonene −90	RF, 100	111.7	80.0	4,5-Epoxinonane (36.0); 4-nonanone (23.0); 5-nonanone (17.0); by-products (24.0)
2-Ethyl-4-methyl-1-hexene, −85	RF, 100	111.7	79.0	2-Ethyl-4-methyl-1, 2-epoxihexane (58.4); 2-ethyl-4-methyl-hexanal (28.6); 5-methyl-3-heptanone (2.0); by-products[b] (11,0)
m-Methyl-styrene −80	RF, 100	111.7	72.2	1,2-Epoxiethyl-m-toluene (41.0); 2-(m-tolyl)-ethanol (39.6); m-tolylethanal (3.1); by-products (16.3)
1-Decene −65	RF, 100	111.7	47.0	1,2-Epoxidecane (47.6); decanal (38.0); by-products[b] (14.4)

Table I. continued.

Substrate T(°C)	Source, power (W)	Oxygen flow rate (mMol/h)	Total conversion[a] (%)	Products (%)
2-Isopropyl-3-methyl-1-butene, –90	RF, 100	111.7	34.5	2-Isopropyl-3-methyl-1,2-epoxibutane (57.0); 2-isopropyl-3-methyl-butanal (13.2); 2,4-dimethyl-3-pentanone (14.1); by-products[b] (15.7)
2,4,4-Trimethyl-1-pentene, –90	RF, 100	111.7	27.3	2,4,4-Trimethyl-1,2-epoxipentane (59.5); 2,4,4-trimethyl-pentanal (29.5); 4,4-dimethyl-2-pentanone (5.7); by-products[b,c] (5.3)

[a]Time of reaction was 30 min for high voltage (hv) and 60 min for radio frequency (RF) experiments.
[b]By-products are mixtures of ketones and carboxylic acids.
[c]Gaseous products represent 2.9%. Oxidation products of 6 to 7 carbon atoms were also observed.

radicals, are the main products.[28] From the point of maximum conversion to lower temperatures the reactivity decreases. At this stage the hydrocarbon is nearly frozen and, hence, the interaction becomes one between oxygen and a solid. It is well known that the reactivity in this case is negligible.[25,28]

Table I summarizes the results for all the compounds. The power source, either high-voltage (hv) or radio frequency (RF), as well as the applied power are indicated. The table also shows the temperature of the liquid for optimum conversion, the oxygen flow rate, the conversion rate, and the product distribution. In order to find a correlation between the reactivities of the different olefins and their structures, the compounds have been arranged in decreasing order of conversion; all conditions have been fixed for each of the systems, except for temperature. Each substrate has been cooled down to a temperature close to its freezing point. Under this condition, for most of the olefins, the products are solids, thus producing high viscosity, which, in turn, has introduced difficulties in stirring the liquid, especially at the end of each experiment.

The results shown in Table I confirm that the reaction of O(^{3}P) with olefins is improved when an alkyl group is attached to the carbon–carbon double bond.[35–37] That is the case if we compare 2-methyl-1-nonene and 2-methyl-1-octene with 1-decene. A group with a positive inductive effect stabilizes the transition diradical,[21,22] thus increasing the reaction rate. On the other hand, the conversions of 2-butyl-1-hexene, 2-ethyl-1-octene, and 3-ethyl-1-heptene are both close to 85%; this seems to indicate that the size of the group does not substantially affect the reactivity. This, in turn, depends

upon the position of the double bond in the carbon chain. As a matter of fact, a mixture of *cis*- and *trans*-4-nonene reacts faster than 1-decene. The two alkyl groups stabilize the transition state. Here, the higher yield of 4-nonanone against 5-nonanone confirms that the O(^{3}P) addition preferentially occurs on the less substituted carbon of the double bond.[12–15,38–40]

The results in Table I also reveal the steric effects of bulky groups, attached to the double bond, on the reaction rate. 2-Isopropyl-1-methyl-1-butene and 2,4,4-trimethyl-1-pentene were oxidized only 35 and 27%, respectively, with the oxygen RF plasma during 1 hr, while 2-methyl-1-nonene and 2-methyl-1-octene reacted nearly 100% at the same conditions.

It has been observed that the main products in the oxidation of the olefins are the corresponding epoxides. The ratio epoxide/carbonyl compounds ranges from 1.0 to 2.0, with the exception of 2-isopropyl-3-methyl-1-butene where the proportion is 4.3. It is clear that the ring closure of the triplet diradical to produce the epoxide is less energetic than the migration of a hydrogen atom to produce the carbonyl compound.

For most of the olefins, a series of experiments has been performed by keeping all parameters fixed except for the time of reaction. It has been observed that the longer the time, the lower the amount of aldehyde, and the higher the amount of the corresponding carboxylic acid. It is clear that the acid is produced from the oxidation of the aldehyde by the oxygen plasma. Similarly, for several olefins, after 15 min of reaction, either the 2-ketone or the 3-ketone represents only 1% of the total, whereas, after 60 min, it is about 10%. We can then deduce that the ketone is produced from the epoxide.
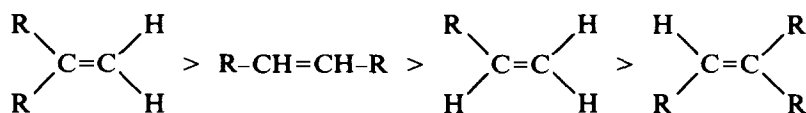
The vapor pressures of four olefins at their optimum temperatures (shown in Table I), calculated by extrapolation of reported values ($\log_{10} p$ versus $1/T$), are as follows: 1-decene, 2.2×10^{-4} Torr at $-65°C$; 2-methyl-1-nonene, 1×10^{-3} Torr at $-64°C$; 1-dodecene, 1.6×10^{-3} Torr at $-32°C$; 1-tetradecene, 1.1×10^{-3} Torr at $-11°C$. These data give the following values for the ratio $p(O_2)/$(vapor pressure of olefin): 7000, 1600, 181, and 264, respectively, thus indicating the importance that this ratio is maintained as high as possible in order to avoid reactions in the gas phase and, hence, to obtain optimum reactivity of O(^{3}P) with these compounds. For the rest of the olefins it is higher than 20, in agreement with the observations for several alkanes and monosubstituted aromatic compounds.[25,33]

4. CONCLUSIONS

It is known that, when atomic oxygen reacts with olefins in the gas phase, the attack at the double bond is only 10 times faster than at the

individual CH bond.[7] For a compound, such as 1-octene, under such conditions, only 38% of the products would come from reaction at the double bond. In the plasma oxidation of liquid olefins, almost all identified products result from this attack. Neither tar nor fragmentation products were observed in the high-voltage device. Less than 3% of gaseous products were observed with one compound, 2,4,4-trimethyl-1-pentene, in the RF system. Oxidation products of C-6 and C-7 were also obtained with this olefin, thus indicating that, at some extension, there was reaction in the gas phase. This is, as a matter of fact, the most volatile of all the olefins oxidized by the oxygen plasmas in this work.

In the reaction of $O(^3P)$ with olefins in the liquid phase, the effect of the olefin structure on the reaction rate has been observed. The high conversions obtained in this study can be explained on grounds of the stabilization of the diradical transition state through the alkylic substitution in the molecule, especially on the double bond. From the results, the following series of reactivity is established.

$$\begin{array}{ccc} \text{R}\diagdown\diagup\text{H} & & \text{R}\diagdown\diagup\text{H} \qquad \text{H}\diagdown\diagup\text{R} \\ \text{C=C} & > \text{R--CH=CH--R} > & \text{C=C} \qquad > \qquad \text{C=C} \\ \text{R}\diagup\diagdown\text{H} & & \text{H}\diagup\diagdown\text{H} \qquad \text{R}\diagup\diagdown\text{R} \end{array}$$

However, due to steric effects, the reaction rate decreases as the size of alkyl group attached to the double bond is larger.

The ratio epoxide/aldehyde is especially favorable at low temperatures, probably as a consequence of the rapid quenching of the primary adduct. These results confirm that the selectivity of such systems is better than that of the gas-phase reactions. In addition, the high yields make the plasma oxidation of liquid olefins attractive for synthesis of epoxides.

ACKNOWLEDGMENTS

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